

Effects of Compositions of Boroxine Polymers on Electrochemical Properties of PEO-based Electrolyte Systems

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Abstract: A family of boroxine polymers (BP) containing different length of side ether chains was synthesized. The addition of BP to PEO/lithium salt system formed anion trapping polymer electrolytes. The influence of the compositions of BP on ionic conductivity, interfacial performance, lithium ion transference number and electrochemical stability of the electrolyte was investigated. Positive effects were obtained for this type of boroxine ring containing compound. Reasons for these effects are also discussed.

Keywords: PEO, Polymer electrolyte, Boroxine polymer, Composite cathode, Lithium anode

1. INTRODUCTION

Solid polymer electrolytes, normally formed by dissolving weakly ion paired lithium salt in high molecular weight host polymer, have attracted much attention because of their combination of electrochemical and mechanical properties¹⁻³. Poly(ethylene oxide) (PEO) based lithium ion conducting polymer electrolytes have been widely studied. The inherently low mobility of charge carrier species in PEO electrolytes at ambient temperature resulted from PEO crystallization is the main limitation for industry application⁴. Many efforts have been devoted to decrease the crystallinity and glass transition temperature (T_g) for enhancement of segment motion of host polymer, including copolymerizing short PEO chain with other monomers⁵⁻⁷, blending PEO with other macromolecules^{8,9}, adding plasticizer or liquid electrolyte to form gel system¹⁰⁻¹², and introducing inorganic additives to produce hybrid electrolytes¹³. In spite of the effectiveness of these methods in improvement of ionic conductivity, gel system works at the cost of mechanical strength, hybrid electrolyte always suffers interfacial problem. For a polymer electrolyte, an additive being effective in improving some electrochemical properties but almost having no other bad effects is greatly favored.

In this work, a series of boroxine polymers (BP) were synthesized and applied in PEO system. The mechanical property was not greatly affected. The effects of the compositions of BP on the electrochemical properties of resultant electrolytes were discussed.

2. EXPERIMENTAL

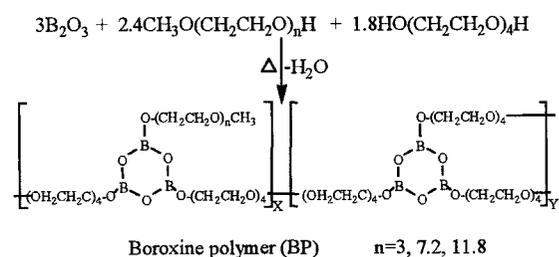
2.1 Materials

Oligoethers: Poly(ethylene glycol) monomethyl ether (PEGMME, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, ($n=3, 7.2, 11.8$)) and tetraethyleneglycol (TEG), (Aldrich), were dried by dry nitrogen bubbling under partial vacuum at room temperature for at least 24h and stored over molecular sieves prior to use. PEO (Aldrich, $M_w 5 \times 10^6$), all lithium salts and solvents were rigorously dried before use. Boric oxide (Merck) was used as supplied. Unless otherwise stated, all manipulations were carried out on a dry nitrogen/vacuum line or in an argon-filled glovebox for exclusion of moisture.

2.2 Synthesis

The synthetic method for BP was previously reported by our laboratory (Scheme 1)¹⁴. In this work, PEGMME with different length of EO chain ($-\text{CH}_2\text{CH}_2\text{O}-$)_n ($n=3, 7.2, 11.8$) were introduced. Three BP differed in the length of side chains were prepared. They appeared as viscous liquids at ambient temperature and were denoted as BP(3), BP(7.2), and BP(11.8) respectively. IR spectra verified the existence of boroxine ring structure: $\sim 719 \text{ cm}^{-1}$, B-O ring vibration; $\sim 1334 \text{ cm}^{-1}$, B-O ring stretching¹⁵. No residue $-\text{OH}$ being determined confirmed complete reaction of all alcohols.

Polymer electrolytes were prepared by dissolving BP, PEO and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (LiTFSI) in dried acetonitrile. Removal of solvent gave the solid polymer electrolytes. Since the maxima of ionic conductivity of PEO based electrolyte is often observed in the region of $\text{EO}:\text{Li}^+ = 15\sim 20:1$, unless otherwise stated, the ratios of $\text{EO}:\text{Li}^+$ (by mole) and PEO:BP (by weight) were fixed to 20:1 and 9:1 respectively in the above-prepared electrolytes.



Scheme 1 Synthetic process for boroxine polymer

2.3 Cathode preparation

PEO and lithium salts (90wt% of LiTFSI and 10wt% of LiPF_6) ($\text{EO}:\text{Li}^+ = 20:1$, working as binder) were dissolved in acetonitrile to get a homogeneous solution. $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and acetylene black first ground in a mortar, were added slowly to the above solution. The mixture was vigorously stirred for 24h and treated with ultrasonic wave for 1h. After removal of part of solvent, the obtained slurry was cast on aluminum substrates. The samples were dried and pressed into thin films to get black composite cathodes. The composition of the composite cathode in weight ratio was controlled as:

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$: composite electrolyte: acetylene black = 65:20:15.

2.4 Characterization

Ionic conductivities were determined by ac impedance measurement in the frequency of 1MHz-1Hz (signal amplitude 10mV) using a Solartron 1260 frequency response analyzer and 1287 electrochemical interface. Interfacial resistances were determined using a similar process for samples sandwiched between non-blocking lithium electrodes. Lithium ion transference numbers (T^+) were determined for samples sandwiched in lithium electrodes using the combined ac impedance/dc polarization method of Evans¹⁶ modified by Abraham¹⁷. Electrochemical stability window was determined by cyclic voltammetry of samples on a Pt working electrode and a lithium reference and counter electrode at a scan rate of 10 mV/s at 60 °C using a Solartron 1287 electrochemical interface. IR spectra were recorded on a Jasco FT/IR-7000 IR spectrometer. Thermal behaviors of polymer electrolytes were investigated by differential scanning calorimeter (DSC) using a Perkin-Elmer Pyris 1 DSC. Heat-cool-reheat cycles were performed at a rate of 10 °C/min in the region of -100~200 °C. All thermal events were reported for the reheating cycle.

3. RESULTS AND DISCUSSION

3.1 Ionic conductivity

In PEO electrolytes, lithium ion transference prompted by segment motion primarily takes place in amorphous phase¹⁸. Low T_g and crystallinity of host polymer leading to high mobility segments and large proportion of amorphous phase are favorable for electrolytes. The effect of addition of 10wt% of BP in PEO/LiTFSI on the thermal characteristics of electrolyte was studied by DSC method (Table I). T_g was not obviously affected by the introduction of BP, while melting point (T_m) and crystallinity (χ) were decreased due to more defects resulted from the interaction between BP and PEO.

Figure 1 shows the temperature dependence of ionic conductivities for PEO/BP/LiTFSI and PEO/LiTFSI electrolytes. At ambient temperature, electrolytes in presence of BP exhibited higher ionic conductivities than PEO/LiTFSI. It is ascribed to the ability of BP in depressing PEO crystallization. When temperature was increased over T_m of PEO, completely amorphous electrolytes were obtained, comparable conductivities were observed for all systems. According to the reaction ratio of reagents, the molecular weights of BP(3), BP(7.2) and BP(11.8) are not high enough to entangle with PEO chain to affect PEO crystallization process. They mainly worked as plasticizers. Because of similar structures and polarities, comparable effects on decrease of crystallinity of PEO were suggested, which was proved by χ values from DSC measurement. Thus, similar effects on enhancement of ionic conductivity for BP(3), BP(7.2) and BP(11.8) were observed.

Table I Thermal characteristics of polymer electrolytes

Electrolytes	T_g (°C)	T_m (°C)	$\Delta H/W$ (J/g)	χ
PEO/LiTFSI	-27.6	63.3	125.7	0.59
PEO/BP(3)/LiTFSI	-28.7	58.2	101.7	0.48
PEO/BP(7.2)/LiTFSI	-29.4	58.2	100.8	0.47
PEO/BP(11.8)/LiTFSI	-28.9	59.4	101.3	0.47

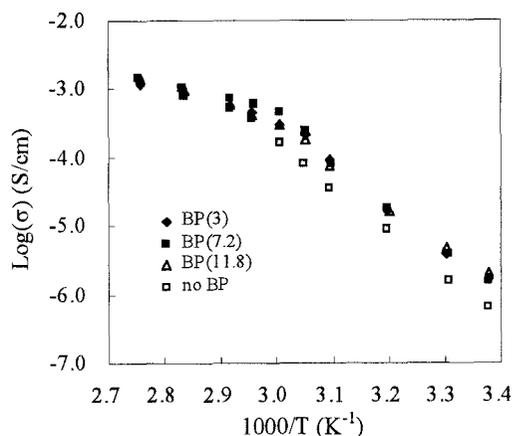


Fig. 1. Ionic conductivities of PEO/LiTFSI and PEO/BP/LiTFSI; EO:Li⁺=20:1, PEO:BP=9:1

3.2 Interfacial resistance (R_{int})

Due to the high reactivity of lithium metal and lithium ion, some complex reactions between electrolyte and electrode take place, leading to the formation of high resistance passivation layer on the surface of electrode¹⁹. In some cases, interfacial resistance is more than 10 times higher than bulk resistance of electrolyte. In order to obtain a lithium secondary battery with long calendar life and cycle life, good compatibility with electrode is a major factor to be considered for electrolyte development. We first investigated the effect of BP with different length of side chains on interfacial resistance on lithium anode at 70 °C. Results shown as time dependence of R_{int} are illustrated in Figure 2. All electrolytes in presence of BP exhibited much lower R_{int} than pure PEO system. An increase of R_{int} from 490 $\Omega\cdot\text{cm}^2$ to 660 $\Omega\cdot\text{cm}^2$ after 200h of testing was observed for PEO/LiTFSI electrolyte. However, BP containing electrolytes behaved in a completely different way, resistances first decreased in a distinct manner and maintained stable during the follow storage period at about 13, 25, and 45 $\Omega\cdot\text{cm}^2$ respectively for PEO/BP(3)/LiTFSI, PEO/BP(7.2)/LiTFSI, and PEO/BP(11.8)/LiTFSI. Compared with pure PEO system, about 50 times lower R_{int} was achieved for PEO/BP(3)/LiTFSI electrolyte. Since the ac response of the interface was observed to be a distorted semi-cycle at low frequency, a proper equivalent circuit²⁰ composed of three parallel combinations of resistance and capacitance,

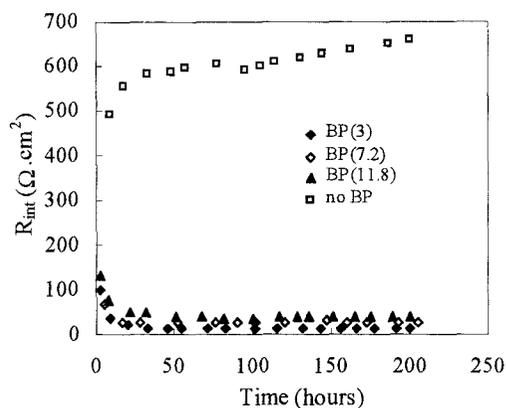


Fig. 2. R_{int} of PEO/LiTFSI and PEO/BP/LiTFSI on lithium anode at 70 °C; EO:Li⁺=20:1, PEO:BP=9:1

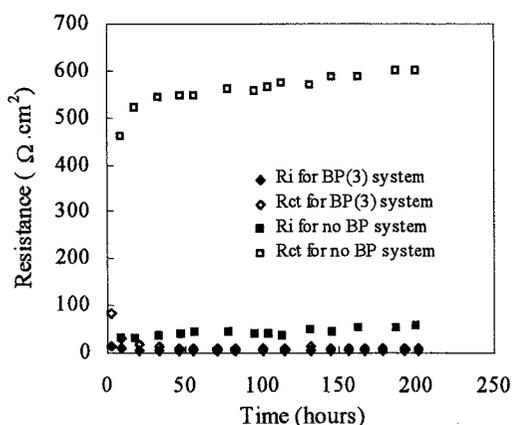


Fig. 3. R_i and R_{ct} of polymer electrolytes on anode at 70°C

corresponding to three stages of lithium ion transport in the cell: transport in electrolyte, transport in passivation layer and transfer from passivation layer to electrode, was applied to refine the analysis of interfacial performance to explore the reason for such effect of BP. Bulk resistance (R_b), passivation film resistance (R_i) and charge transfer resistance (R_{ct}) were obtained by fitting impedance spectra to the equivalent circuit. Figure 3 shows the fitting results of R_i and R_{ct} as a function of time. R_i of PEO/LiTFSI initially determined as 28 $\Omega\cdot\text{cm}^2$ was duplicated after 200h of testing at 70°C, leading to an increase of R_{ct} from 460 $\Omega\cdot\text{cm}^2$ to 600 $\Omega\cdot\text{cm}^2$. It was related to the formation of high resistance passivation film on lithium anode. As to PEO/BP(3)/LiTFSI electrolyte, R_i was decreased from 15 $\Omega\cdot\text{cm}^2$ to 3 $\Omega\cdot\text{cm}^2$ in the first 25h and kept practically constant thereafter, indicating that BP contributed not only to the formation of low resistance passivation film, but also to the depression of build-up of high resistance film caused by the degradation of electrolyte. Zhang et al.²¹ reported the stabilizing effect of boric acid esters of glycols on liquid electrolyte/Li interface. The formation of single ion conducting film composed of amorphous LiBO_2 on the surface of lithium metal was proposed for this effect. Because of the existence of such boric ester structure in BP, we also attribute the effect of BP on lowering and stabilizing R_{int} to the formation of LiBO_2 composed protective film on lithium negative electrode. Short-side-chain BP exhibiting better performance in decreasing R_{int} than long-side-chain BP was obviously

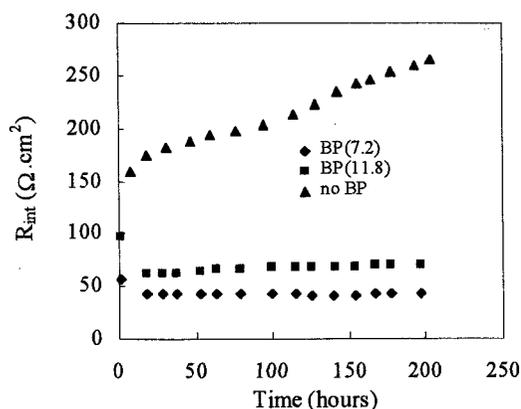


Fig. 4. R_{int} of PEO/LiTFSI and PEO/BP/LiTFSI on composite cathode at 70°C; EO:Li⁺=20:1, PEO:BP=9:1

seen. BP(3) containing electrolyte showed about 4 times lower R_{int} than BP(11.8) containing counterpart. It was related to the steric effect of side chains. Since LiBO_2 structure was formed by contacting lewis acid center in BP (boron atom) with lithium metal, long side chains are great barriers for the meet of B with Li. In addition, compared with short-side-chain BP, the inherently lower mobility of long-side-chain BP makes it more difficult to diffuse to the electrolyte/Li interface. Therefore, a relatively higher R_{int} was obtained for PEO/BP(11.8)/LiTFSI electrolyte.

Compatibility with cathode is another important factor to be considered. Recently Amine et al.²² studied high power 18,650 cells consisted of a $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ positive electrode, a carbon negative electrode and a LiPF_6 in EC-PC (1:1) electrolyte. They found that the power fade of the cells caused by a significant impedance rise was primarily due to the increase of interfacial resistance on the positive electrode. In this work, a composite cathode using $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ as active material was prepared. An investigation of the effect of BP with different length of side chains on R_{int} on the surface of cathode was performed at 70°C. Figure 4 shows a significant increase in R_{int} from 160 $\Omega\cdot\text{cm}^2$ in the fresh cell to 260 $\Omega\cdot\text{cm}^2$ after 200h of testing for PEO/LiTFSI. R_{int} of PEO/BP(7.2)/LiTFSI and PEO/BP(11.8)/LiTFSI initially determined as 55 $\Omega\cdot\text{cm}^2$ and 98 $\Omega\cdot\text{cm}^2$ experienced sharp breaks in the first 20h, then increased slowly in the following 120h and maintained stable at about 42 $\Omega\cdot\text{cm}^2$ and 70 $\Omega\cdot\text{cm}^2$ respectively. BP containing electrolytes all show much lower and more stable R_{int} than pure PEO system. Short-side-chain BP exhibiting better performance on electrolyte/cathode interface than long-side-chain BP is obviously seen. As the reason for such effect of BP is still unknown, R_i and R_{ct} were obtained (Figure 5) by fitting impedance spectra to the equivalent circuit above described. R_i of PEO/LiTFSI increased from 38 $\Omega\cdot\text{cm}^2$ to 74 $\Omega\cdot\text{cm}^2$ after being annealed at 70°C for 200h indicating the formation of high resistance passivation film. Electrolytes in the presence of BP exhibiting much lower R_i and R_{ct} was ascribed to the existence of low resistance interface film on cathode. A decrease in R_i in the first several hours leading to an acute decrease in R_{ct} was a good proof for the formation of such low resistance film. However, unlike the phenomenon observed on lithium anode, on BP containing electrolyte/composite cathode interface, R_i didn't maintained constant but experienced a period of

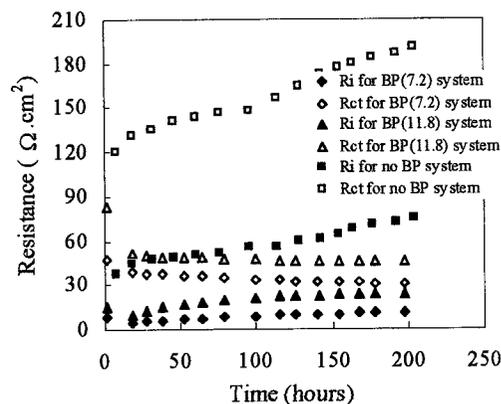


Fig. 5. R_i and R_{ct} of polymer electrolytes on cathode at 70°C

increase after the formation of low resistance passivation film and then kept stable thereafter, indicating that some corrosion process unable to be effectively hindered by BP occurred. Lower R_i and R_{ct} were observed for PEO/BP(7.2)/LiTFSI than for PEO/BP(11.8)/LiTFSI. Higher mobility and easier contact with cathode particles leading to larger coverage of low resistance passivation layer on composite cathode surface accounts for such effect of short-side-chain BP. Although the cathode discussed here is equivalent to that in discharging state and it may be more active in charging state, we still can see that BP is effective to enhance the compatibility between PEO/LiTFSI electrolyte and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode.

3.3 Lithium ion transference number (T^+)

Electron deficiency property of boroxine ring in BP enables it to work as an anion trapping compound. Due to the large volume of BP-anion complex, the motion of anion is believed to be somewhat hindered, which will lead to the improvement of T^+ . Table II shows the effect of BP with different length of side chains on this property. Higher T^+ was observed for BP containing electrolytes. 3 times higher T^+ was determined for PEO/BP(11.8)/LiTFSI than for pure PEO system. Long-side-chain BP exhibited better performance in enhancement of T^+ than short-side-chain BP. Lower mobility of long-side-chain BP-anion complex accounts for this result.

Table II T^+ of polymer electrolytes at 70°C

Electrolytes	T^+
PEO/LiTFSI	0.05
PEO/BP(3)/LiTFSI	0.06
PEO/BP(7.2)/LiTFSI	0.08
PEO/BP(11.8)/LiTFSI	0.15

3.4 Electrochemical stability window

A wide range of electrochemical stability window is essential for applicable polymer electrolyte. Figure 6 shows the cyclic voltammetry of PEO/LiTFSI and PEO/BP/LiTFSI systems on a Pt working electrode at a scan rate of 10mV/s. Because of the low conductivities of these polymer electrolytes at ambient temperature, the determination was performed at 60 °C. An electrochemical stability window of approximately 4.7V versus Li/Li^+ was obtained for PEO/LiTFSI. PEO/BP(3)/LiTFSI, PEO/BP(7.2)/LiTFSI and PEO/BP(11.8)/LiTFSI showed the stability window of

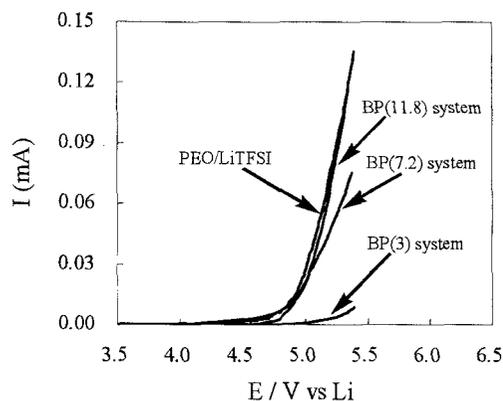


Fig. 6. Cyclic voltammety of polymer electrolytes at a scan rate of 10mV/s at 60°C

about 5.0V, 4.8V and 4.7V respectively. No significant effect of BP on this property was observed. A slightly better performance in extending stability window was obtained for BP(3). These results ensured the safe application of BP in PEO based electrolyte with no harm to electrochemical stability.

CONCLUSION

A series of BP with different length of side chains have been simply prepared. The addition of BP into PEO based polymer electrolyte improves ionic conductivity, lithium ion transference number, and interfacial performance. BP with different length of side chains shows similar effect on enhancement of ionic conductivity at low temperature. Long-side-chain BP is more effective in increasing lithium ion transference number. Short-side-chain BP decreases interfacial resistances remarkably on the surfaces of both lithium anode and composite cathode and slightly improves the electrochemical stability of the electrolyte.

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